Vapor−Liquid Equilibrium for Methanol + 1,1-Dimethylpropyl Methyl Ether at (288.15, 308.15, and 328.15) K

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Vapor−liquid equilibria for methanol + 1,1-dimethylpropyl methyl ether (*tert*-amyl methyl ether or TAME) have been measured at (288.15, 308.15, and 328.15) K. A Gibbs−Van Ness type apparatus for total vapor pressure measurements has been used. The system shows positive deviations from Raoult's law with an azeotrope, whose coordinates are reported at the three temperatures studied. Results have been analyzed in terms of the UNIQUAC model, several versions of the UNIFAC model, and the modified-Huron−Vidal second-order (MHV2) group contribution equation of state.

Introduction

Oxygenated compounds are being used as additives to gasoline because of their antiknock effects. 1,1-Dimethylpropyl methyl ether (*tert*-amyl methyl ether or TAME) appears to be a good candidate as a gasoline-blending agent (Ignatius et al., 1995). This ether is produced by the reaction of methanol and 2-methyl-2-butene or 2-methyl-1-butene (Chase and Galvez, 1981). In order to design the separation unit, detailed information about the vapor−liquid equilibria (VLE) is of great industrial interest. However, VLE for the mixture methanol + TAME are very scarce in the literature and were only measured under atmospheric pressure (Cervenkova and Boublik, 1984; Evans and Edlund, 1936; Pavlova et al., 1981; Palczewska-Tulinska and Wyrzykowska-Stankiewicz, 1990). The purpose of this paper is to report VLE data for methanol + TAME measured at three temperatures and to discuss these data in terms of the UNIQUAC and UNIFAC models and a group contribution equation of state.

Experimental Section

Materials. TAME (FLUKA 97% purity) was fractionally distilled over molecular sieves for several hours. The middle distillate used in the present work (approximately 50% of the initial amount) had a purity better than 99.6%, as measured by a gas chromatographic analysis. Methanol was from CARLO ERBA (RPE quality), with a purity higher than 99.9%. Both components were handled under a dry nitrogen atmosphere and were degassed by reflux distillation for several hours, as previously described by Coto et al. (1995).

Apparatus and Procedure. Experimental VLE were measured using a Gibbs−Van Ness type static apparatus (Gibbs and Van Ness, 1972). A detailed description of the apparatus, the experimental method, and the data reduction procedure has been described elsewhere (Coto et al., 1995). Binary liquid solutions of known composition were prepared in a test cell with a total volume of about 100 cm^3 by volumetric injection of degassed liquids using calibrated pistons. The accuracy of the mole fraction is estimated to be about 0.0001 in the dilute regions and about 0.0003 in the middle of the concentration range. Cell and piston injectors were immersed in a water bath in which the temperature was controlled within ±0.002 K. The temperature was monitored with a quartz thermometer, Hewlett-Packard 2804A, with an accuracy of 0.01 K. The total vapor pressure was measured when phase equilibrium was reached using a differential MKS Baratron pressure gauge with a resolution of 0.08% of the reading. Calibration was made using a mercury manometer of 8 Pa precision, as has been described elsewhere (Coto et al., 1995). Pressure accuracy is estimated to be 0.01 kPa. A complete isothermal data set was obtained after two experimental runs. Each was started by injecting about 6 cm^3 of one of the components, followed by consecutive injections of small amounts of the second component until an equimolar mixture was obtained. The order of mixing of the two components was reversed in the second run to cover the second part of the composition range.

Table 1. Pure Component Properties Used in This Study

	T/K	B/cm^3·mol^{-1}	v/cm^3·mol^{-1}	β/10^{-9} Pa^{-1}
methanol	288.15	−2295	40.254	1.170
	308.15	−1735	41.228	1.336
	328.15	−1321	42.249	1.521
TAME	288.15	−2549	131.78	
	308.15	−2064	135.13	
	328.15	−1714	138.67	

Table 1 lists the values for the molar volumes, isothermal compressibilities, and second virial coefficients for the pure components. For methanol, molar volumes were taken from Timmermans (1950, 1965) and second virial coefficients were taken from Dymond and Smith (1980). Isothermal compressibilities were reported by Díaz Peña and Tardajos (1979), and the value at 328.15 K was extrapolated from these data. Molar volumes for TAME were measured at (298.15, 308.15, and 318.15) K by Cancho (1995), and molar volume values at (288.15 and 328.15) K were obtained by extrapolation of these data. Second virial coefficients were estimated by the method of Hayden and O'Connell (1975).

The measured vapor pressures for methanol are in good agreement with literature values (Gmehling et al., 1977, 1982). TAME vapor pressure data are scarce (Antosik and Sandler, 1994; Cervenkova and Boublik, 1984; Palczewska-Tulinska et al., 1984; Semar et al., 1995). The vapor pressure data obtained in this study for TAME in the (288.15 to 328.15) K temperature range are in good agreement with those reported by Cervenkova and Boublik (1984). The agreement with data reported by Palczewska-Tulinska et al. (1984) is fair (Figure 1). No comparison is

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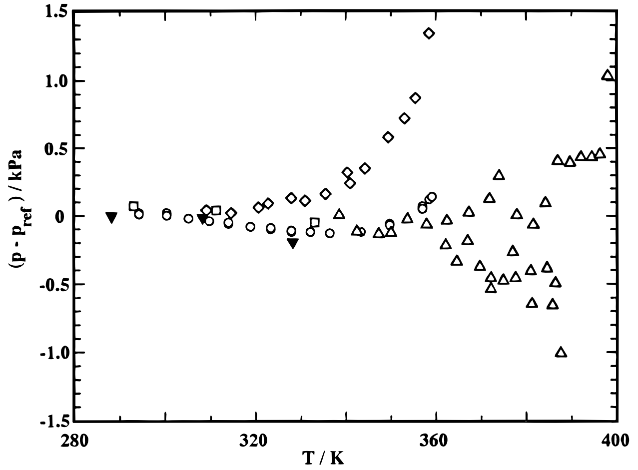

Figure 1. Deviation between experimental vapor pressure data and those calculated using eq 1 for TAME: (○), Cervenkova and Boublik, 1984; (□) Antosik and Sandler, 1994; (△) Semar et al., 1995; (◇) Palczewska-Tulinska et al., 1984; (▼) this work.

Table 2. Antoine Equation Coefficients for TAME

	A	B	C	T/K	σ_p/kPa
TAME	5.83173	1131.03	209.145	288−398	0.36

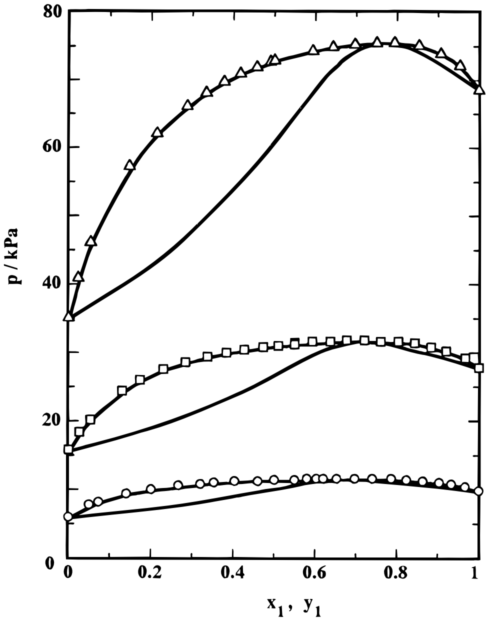

Figure 2. VLE data for the methanol (1) + TAME (2) system: (○) 288.15 K; (□) 308.15 K; (△) 328.15 K; (—) calculated values.

possible with the data reported by Semar et al. (1995) because the temperature ranges do not overlap. The reference pressures were calculated by means of the Antoine equation which is given by

$$\log_{10}(p/\mathrm{kPa}) = A - \frac{B}{C + (t/°\mathrm{C})} \tag{1}$$

Values for the coefficients A, B, and C were obtained from the values reported here and from literature values (Antosik and Sandler, 1994; Cervenkova and Boublik, 1984; Palczewska-Tulinska et al., 1984; Semar et al., 1995) and are listed in Table 2.

Results and Discussion

The VLE measurements for methanol + TAME were made at (288.15, 308.15, and 328.15) K. Results were analyzed using Barker's method (Barker, 1953) and the maximum likelihood principle (Anderson et al., 1978; Rubio et al., 1983). The temperature, T, and the amounts (in mole) of components 1 and 2 were considered to be the independent variables in the data reduction. A material balance was done to take into account the material present in the vapor phase.

The excess Gibbs energy, G^E, of the liquid phase was assumed to be described by an (m/n) Padé approximant and is given by

$$\frac{G^E}{RT} = x_1(1 - x_1)\frac{\sum_{i=0}^{m} P_i(2x_1 - 1)^i}{1 + \sum_{j=1}^{n} Q_j(2x_1 - 1)^j} \tag{2}$$

where P_i and Q_j are constants and x_1 is the mole fraction of methanol. The best results in the data reduction were obtained when the Q_j constants were set equal to zero. This makes eq 2 equivalent to the Redlich−Kister equation. The vapor phase is described using the virial equation, and the values of the second virial coefficients are given in Table 1. Values for the second cross virial coefficient were calculated using pure component values and a cubic combination rule. The effect of the uncertainty in the virial coefficients on calculated p and x is negligible. A small change in the values of second virial coefficients does not lead to a significant change in the final results.

Table 3 lists values for the methanol liquid composition, x_1, and the total pressure, p, obtained in the present work at each of the three temperatures studied. Table 3 also shows the calculated total pressure, p_{calc}, the alcohol vapor composition, y_1, G^E, the activity coefficients, γ_1 and γ_2, for the methanol and TAME, respectively, the Padé coefficients, P_i, for G^E representation by eq 2, and the standard deviations between experimental and calculated values of x_1, σ_x, and p, σ_p. Values for the standard deviations σ_x and σ_p are in agreement with the experimental uncertainties given in the Experimental Section. This is an indication of the thermodynamic consistency for the data. These results are plotted in Figure 2. Deviations from Raoult's law are positive and an azeotrope is exhibited at the three temperatures studied. The azeotrope becomes more pronounced as the temperature increases. Figure 3 uses an extended scale at (288.15 and 308.15) K, and the existence of the azeotrope is clearly shown.

The interpolated azeotrope coordinates at the three temperatures studied are listed in Table 4. Figure 4 is a plot of temperature versus methanol mole fraction for the azeotropes. Uncertainties in the azeotrope coordinate values are of approximately ±0.003 in the liquid mole fraction, and of lower than 0.25% in the pressure. The values reported in the literature (Cervenkova and Boublik, 1984, Evans and Edlund, 1936; Pavlova et al., 1981; Palczewska-Tulinska and Wyrzykowska-Stankiewicz, 1990) are also included in the plot. The literature data were obtained from isobaric VLE measurements at atmospheric pressure and cannot be directly compared to the data reported in this study, nevertheless, the azeotrope coordinates here reported seem to be in good agreement with those reported by Cervenkova and Boublik (1984), Palczewska-Tulinska and Wyrzykowska-Stankiewicz (1990), and Pavlova et al. (1981). The agreement between the oldest

Table 3. Vapor–Liquid Equilibrium Data and Coefficients and Standard Deviations for G^E Description by Eq 2 for Methanol (1) + TAME (2) at (288.15, 308.15, and 328.15) K

x_1	p/kPa	p_{calc}/kPa	y_1	G^E/J·mol^{-1}	ln γ_1	ln γ_2	x_1	p/kPa	p_{calc}/kPa	y_1	G^E/J·mol^{-1}	ln γ_1	ln γ_2
288.15 K													
0.0000	6.09	6.09	0.0000	0		0.0000	0.6043	11.56	11.56	0.6573	814	0.2413	0.4905
0.0488	7.72	7.68	0.2405	168	1.3464	0.0045	0.6208	11.60	11.57	0.6625	804	0.2235	0.5187
0.0741	8.24	8.28	0.3099	246	1.2581	0.0103	0.6545	11.61	11.59	0.6732	776	0.1881	0.5811
0.1410	9.38	9.39	0.4202	427	1.0439	0.0360	0.6960	11.60	11.59	0.6869	731	0.1471	0.6663
0.1986	10.00	10.00	0.4748	552	0.8853	0.0683	0.7397	11.58	11.57	0.7031	669	0.1077	0.7667
0.2678	10.51	10.50	0.5201	670	0.7262	0.1165	0.7856	11.51	11.51	0.7241	588	0.0717	0.8824
0.3207	10.80	10.78	0.5477	738	0.6242	0.1590	0.8245	11.40	11.41	0.7471	507	0.0464	0.9869
0.3547	10.94	10.94	0.5637	773	0.5663	0.1885	0.8624	11.24	11.26	0.7769	415	0.0269	1.0918
0.4030	11.11	11.13	0.5846	809	0.4920	0.2338	0.9049	10.96	10.98	0.8225	300	0.0116	1.2075
0.4596	11.27	11.30	0.6072	835	0.4140	0.2929	0.9336	10.71	10.72	0.8633	215	0.0051	1.2814
0.5002	11.36	11.40	0.6223	842	0.3624	0.3406	0.9682	10.35	10.32	0.9265	106	0.0010	1.3605
0.5490	11.46	11.49	0.6392	837	0.3039	0.4051	1.0000	9.86	9.86	1.0000	0	0.0000	
0.5816	11.58	11.53	0.6500	826	0.2665	0.4537							
$P_0 = 1.406 \pm 0.003$; $P_1 = 0.045 \pm 0.008$; $P_2 = 0.17 \pm 0.02$; $P_3 = -0.10 \pm 0.02$; $P_4 = -0.10 \pm 0.04$; $\sigma_x = 0.0004$; $\sigma_p = 20$ Pa													
308.15 K													
0.0000	15.80	15.80	0.0000	0		0.0000	0.5505	31.26	31.29	0.6567	869	0.2890	0.4009
0.0282	18.35	18.32	0.1594	98	1.3185	0.0012	0.5948	31.51	31.49	0.6716	850	0.2401	0.4665
0.0547	20.25	20.31	0.2587	185	1.2419	0.0045	0.6368	31.62	31.62	0.6861	820	0.1975	0.5349
0.1309	24.49	24.44	0.4194	404	1.0349	0.0257	0.6767	31.70	31.70	0.7007	780	0.1602	0.6062
0.1744	26.03	26.04	0.4715	510	0.9270	0.0451	0.7216	31.74	31.73	0.7186	721	0.1222	0.6947
0.2316	27.57	27.59	0.5195	627	0.7974	0.0781	0.7598	31.69	31.69	0.7359	660	0.0932	0.7775
0.2834	28.63	28.63	0.5516	713	0.6914	0.1148	0.8045	31.55	31.55	0.7598	574	0.0635	0.8843
0.3369	29.45	29.44	0.5780	782	0.5930	0.1590	0.8419	31.31	31.32	0.7842	490	0.0425	0.9821
0.3834	30.00	30.01	0.5976	826	0.5154	0.2027	0.8827	30.89	30.90	0.8178	384	0.0240	1.0985
0.4281	30.47	30.45	0.6146	856	0.4475	0.2490	0.9216	30.27	30.27	0.8599	270	0.0109	1.2189
0.4729	30.82	30.81	0.6305	872	0.3853	0.3001	0.9654	29.20	29.18	0.9257	126	0.0022	1.3653
0.5086	31.03	31.06	0.6427	876	0.3393	0.3444	1.0000	27.89	27.89	1.0000	0	0.0000	
0.5513	31.34	31.30	0.6569	869	0.2882	0.4020							
$P_0 = 1.367 \pm 0.001$; $P_1 = 0.033 \pm 0.003$; $P_2 = 0.101 \pm 0.007$; $P_3 = 0.010 \pm 0.007$; $P_4 = -0.023 \pm 0.013$; $\sigma_x = 0.0002$; $\sigma_p = 17$ Pa													
328.15 K													
0.0000	35.27	35.27	0.0000	0		0.0000	0.5014	72.98	72.92	0.6602	890	0.3345	0.3176
0.0248	41.08	40.96	0.1560	94	1.3377	0.0014	0.5917	74.37	74.41	0.6929	867	0.2366	0.4357
0.0549	46.26	46.40	0.2718	199	1.2191	0.0063	0.6444	74.94	75.02	0.7125	829	0.1871	0.5159
0.1471	57.34	57.27	0.4466	463	0.9363	0.0373	0.6951	75.39	75.44	0.7326	775	0.1444	0.6024
0.2135	62.28	62.25	0.5129	608	0.7827	0.0710	0.7513	75.64	75.66	0.7574	693	0.1028	0.7114
0.2870	66.15	66.25	0.5641	732	0.6425	0.1176	0.7942	75.62	75.61	0.7790	615	0.0747	0.8069
0.3334	68.18	68.21	0.5896	791	0.5651	0.1524	0.8540	75.15	75.10	0.8155	480	0.0416	0.9631
0.3776	69.77	69.77	0.6108	835	0.4975	0.1897	0.9070	74.02	73.99	0.8588	334	0.0187	1.1327
0.4160	71.00	70.92	0.6273	862	0.4431	0.2255	0.9529	72.11	72.13	0.9124	182	0.0053	1.3118
0.4573	71.99	71.97	0.6437	881	0.3886	0.2678	1.0000	68.58	68.58	1.0000	0	0.0000	
0.4902	72.71	72.70	0.6561	889	0.3478	0.3045							
$P_0 = 1.304 \pm 0.001$; $P_1 = 0.040 \pm 0.004$; $P_2 = 0.123 \pm 0.009$; $P_3 = 0.004 \pm 0.009$; $P_4 = 0.066 \pm 0.017$; $\sigma_x = 0.0003$; $\sigma_p = 44$ Pa													

Table 4. Experimental and Calculated Azeotrope Coordinates for Methanol (1) + TAME (2) Using Several Models

	288.15 K		308.15 K		328.15 K		101.3 kPa	
	x_1	p/kPa	x_1	p/kPa	x_1	p/kPa	x_1	T/K
Experimental Results								
this work	0.6823	11.59	0.7116	31.73	0.7630	75.66		
Cervenkova and Boublik, 1984							0.7710	335.41
Evans and Edlund, 1936							0.7419	335.45
Pavlova et al., 1981							0.7656	335.29
Palczewska-Tulinska and Wyrzykowska-Stankiewicz, 1990							0.7674	335.37
Model								
UNIQUAC	0.6698	11.58	0.7116	31.60	0.7509	75.34	0.7696	335.65
UNIFAC	0.6941	11.21	0.7367	30.82	0.7795	73.81	0.7966	336.15
mod UNIFAC	0.6723	11.92	0.7100	32.49	0.7496	77.07	0.7636	335.11
new UNIFAC	0.7168	11.57	0.7382	31.60	0.7656	74.93	0.7777	335.80
MHV2 + UNIFAC	0.6773	11.23	0.7177	31.04	0.7587	74.48	0.7742	335.90
MHV2 + mod UNIFAC	0.6580	11.95	0.6939	32.77	0.7322	77.59	0.7451	334.81
MHV2 + new UNIFAC	0.7035	11.59	0.7223	31.83	0.7472	75.77	0.7576	335.53

values reported by Evans and Edlund (1936) and the other values is poor.

Values for the excess Gibbs energy of methanol + TAME are positive, with maxima of (840, 875, and 890) J·mol^{-1} appearing at $x_1 \approx 0.5$ at (288.15, 308.15, and 328.15) K, respectively. The effect of the temperature upon G^E is very small, thus corresponding to a moderate excess enthalpy. An excess enthalpy value of 430 J·mol^{-1} is obtained at $x_1 \approx 0.5$ from the indicated G^E values by means of the Gibbs–Helmholtz equation. This value is in fair agreement with

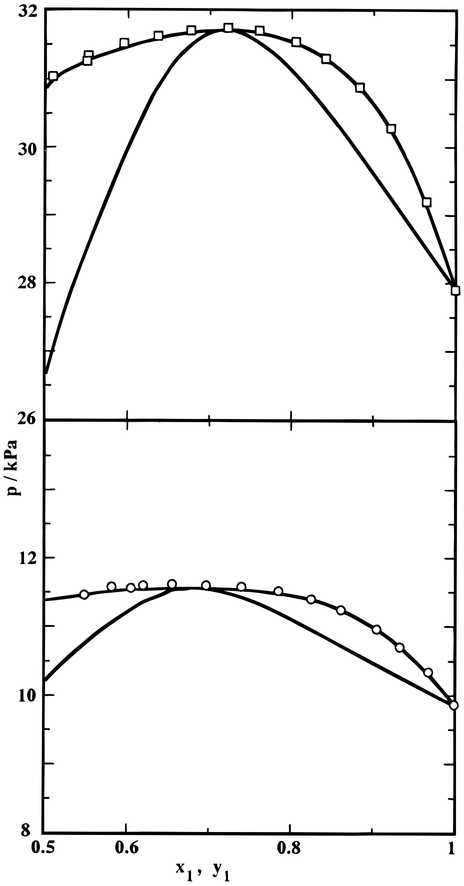

Figure 3. VLE data in the azeotrope region for the methanol (1) + TAME (2) system: (○) 288.15 K; (□) 308.15 K; (—) calculated values.

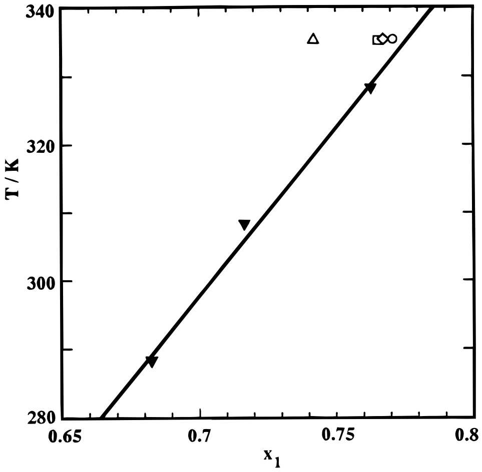

Figure 4. Plot of temperature against x_1 for the azeotrope of methanol (1) + TAME (2): (○) Cervenkova and Boublik, 1984; (□) Pavlova et al., 1981; (△) Evans and Edlund, 1936; (◇) Palczewska-Tulinska and Wyrzykowska-Stankiewicz, 1990; (▼) this work.

the experimental value reported in the literature (H^E = 353 J·mol^{-1} for $x_1 \approx 0.5$ and T = 298.15 K) (Letcher and Govender, 1995).

The UNIQUAC model (Abrams and Prausnitz, 1975) was used to correlate the isothermal VLE data for methanol + TAME reported in this paper. The interaction parameters of this model, A_{ji}, were considered to be dependent on temperature according to the relation

$$A_{ji} = A_{ji,1} + A_{ji,2}(T - T_0) \tag{3}$$

where $A_{ji,1}$ and $A_{ji,2}$ are interaction parameters and T_0 is a reference temperature, taken as 298.15 K. The values for the parameters obtained by means of the maximum likelihood method are $A_{12,1} = -63.86$ K, $A_{21,1} = 454.4$ K, $A_{12,2} = 0.0283$, and $A_{21,2} = 0.2641$.

Vetere et al. (1993) and Coto et al. (1996) have shown that UNIFAC models provide good VLE predictions for methanol + 1,1-dimethylethyl methyl ether (*tert*-butyl methyl ether or MTBE). Similar results may be expected for methanol + TAME. Therefore, calculations were carried out using the UNIFAC (Fredenslund et al., 1977; Hansen et al., 1991), modified UNIFAC (Larsen et al., 1987), and new UNIFAC (Hansen et al., 1992) models. Values for the standard deviations between experimental and calculated vapor compositions, σ_y, and vapor pressures, σ_p, for the UNIQUAC and UNIFAC models mentioned above are given in Table 5.

As could be expected, the best description of the vapor composition and vapor pressure here reported is provided by the UNIQUAC model. σ_p values for this model range from 0.07 kPa at 288.15 K to 0.43 kPa at 328.15 K. The UNIFAC and the modified UNIFAC models provide a good prediction of the vapor phase composition. The σ_y values obtained by means of the new UNIFAC model are slightly worse. However, the new UNIFAC model predicts the vapor pressure better than the two previous UNIFAC versions. σ_p values for the new UNIFAC model range from 0.27 kPa at 288.15 K to 0.82 kPa at 328.15 K.

These models were also used to predict the isobaric data of Cervenkova and Boublik (1984) and Palczewska-Tulinska and Wyrzykowska-Stankiewicz (1990). The values used for the UNIQUAC interaction parameters were those obtained from the isothermal VLE data. Values for σ_y and σ_p are given in Table 5. Values for the standard deviations between experimental and calculated vapor pressures and vapor compositions are substantially higher for data reported by Cervenkova than for data reported by Palczewska.

Calculations using the modified-Huron−Vidal second-order (MHV2) model (Dahl et al., 1991) were also carried out. MHV2 is a combination of the Soave−Redlich−Kwong (SRK) equation of state (Soave, 1972) and a G^E model. The SRK EOS is given by

$$p = \frac{RT}{v - b} - \frac{a}{v(v + b)} \tag{4}$$

For pure components, the parameter a is given by

$$a = 0.4286\,\frac{(RT_c)^2}{p_c}[f(T_r)]^2 \tag{5}$$

where T_c and p_c are the critical temperature and critical pressure, respectively, and $f(T_r)$ is a function of the reduced temperature, T_r, which has been proposed by Mathias and Copeman (1983) and is given by

$$f(T_r) = 1 + C_1(1 - T_r^{1/2}) + C_2(1 - T_r^{1/2})^2 + C_3(1 - T_r^{1/2})^3 \tag{6}$$

where C_1, C_2, and C_3 are the so-called Mathias and Copeman coefficients obtained from vapor pressure data.

Table 5. Standard Deviations between Experimental and Calculated Vapor Composition[a] and Vapor Pressure Values Using the UNIQUAC, UNIFAC, Modified UNIFAC, and New UNIFAC Models for Methanol (1) + TAME (2)

	UNIQUAC		UNIFAC		mod UNIFAC		new UNIFAC		
T/K	σ_y	σ_p/kPa	σ_y	σ_p/kPa	σ_y	σ_p/kPa	σ_y	σ_p/kPa	ref
288.15	0.007	0.07	0.014	0.33	0.013	0.34	0.025	0.27	this work
308.15	0.005	0.11	0.012	0.88	0.011	0.74	0.017	0.55	this work
328.15	0.010	0.43	0.011	1.8	0.011	1.56	0.012	0.82	this work

	UNIQUAC		UNIFAC		mod UNIFAC		new UNIFAC		
p/kPa	σ_y	σ_p/kPa	σ_y	σ_p/kPa	σ_y	σ_p/kPa	σ_y	σ_p/kPa	ref
101.3	0.021	3.8	0.028	5.3	0.014	2.5	0.021	3.9	Cervenkova and Boublik, 1984
101.3	0.004	0.86	0.012	2.6	0.007	1.1	0.006	1.3	Palczewska-Tulinska and Wyrzykowska-Stankiewicz, 1990

[a] For the isothermal data obtained in the present work, σ_y is the standard deviation between calculated vapor compositions and those obtained by means of the Barker method.

Table 6. Critical Temperature, T_c, Critical Pressure, p_c, and the Mathias−Copeman Coefficients

	T_c/K	p_c/MPa	C_1	C_2	C_3
methanol	513.2	7.95	1.4450	−0.8150	0.2486
TAME	531.5	3.11	1.1491	−1.6103	3.3665

The MHV2 mixing rule for the parameter a is expressed as

$$q_1(\alpha_{\text{mix}} - \sum_i z_i\alpha_{ii}) + q_2(\alpha_{\text{mix}}^{\;2} - \sum_i z_i\alpha_{ii}^{\;2}) = \frac{G^{\text{E}}}{RT} + \sum_i z_i \ln \frac{b}{b_{ii}} \quad (7)$$

where α is given by

$$\alpha = \frac{a}{bRT} \quad (8)$$

and z_i is the phase composition (x_i and y_i for the liquid and vapor phases, respectively). Values for q_1 and q_2 were taken from the literature (Dahl et al., 1991): $q_1 = -0.478$ and $q_2 = -0.0047$. Values for G^{E} in eq 7 may be obtained by means of any well-defined G^{E} model. In this work, the UNIFAC model versions already mentioned were used to estimate G^{E} values. The MHV2 model allows the simultaneous prediction of the VLE and other properties such as densities.

Values for the critical temperature and pressure and the Mathias−Copeman coefficients used in this model for the pure components are listed in Table 6. For TAME, values for T_c and p_c were estimated from the Joback method (Reid et al., 1977) and values for C_1, C_2, and C_3 were estimated from experimental vapor pressure data measured in this work and literature values (Antosik and Sandler, 1994; Cervenkova and Boublik, 1984; Palczewska-Tulinska et al., 1984; Semar et al., 1995). For methanol, values for C_1, C_2, and C_3 were taken from literature (Dahl et al., 1991).

The MHV2 model used in conjunction with the original and new UNIFAC models for G^{E} provides a good description of the vapor pressure for methanol + TAME. Values for σ_p are smaller than those obtained when the UNIFAC models were used alone, and the difference increases with the rising temperature. The best prediction of vapor pressure was achieved when the MHV2 + new UNIFAC model was used. σ_p values range from 0.23 kPa at 288.15 K to 0.53 kPa at 328.15 K. The transition from modified UNIFAC to MHV2 + modified UNIFAC leads in most cases to a less accurate prediction for the vapor pressure. As to the vapor compositions, σ_y values obtained by means of the UNIFAC models are of similar magnitude to those obtained by means of the MHV2 + UNIFAC models.

Values for the azeotrope coordinates of methanol + TAME were calculated using the models already mentioned and are listed in Table 4. The azeotrope coordinates interpolated using the UNIQUAC model are in good agreement with the experimental values. It has to be noted that the best prediction of the azeotrope concentration was achieved using the MHV2 + UNIFAC model, while the lowest deviations for the azeotrope vapor pressure were obtained using the MHV2 + new UNIFAC model. In general, good predictions were obtained using the MHV2 in combination with UNIFAC and new UNIFAC models. The accuracy of the predictions of the azeotrope coordinates does not follow the same trend of the standard deviation for y or p listed in Tables 5 and 7.

Table 7. Standard Deviations between Experimental and Calculated Vapor Composition[a] and Vapor Pressure Values Using the MHV2 Model with the UNIFAC, Modified UNIFAC, and New UNIFAC Models for Methanol (1) + TAME (2)

	MHV2 + UNIFAC		MHV2 + mod UNIFAC		MHV2 + new UNIFAC		
T/K	σ_y	σ_p/kPa	σ_y	σ_p/kPa	σ_y	σ_p/kPa	ref
288.15	0.016	0.32	0.015	0.43	0.023	0.23	this work
308.15	0.012	0.64	0.014	1.2	0.014	0.34	this work
328.15	0.010	0.99	0.014	2.8	0.011	0.53	this work

	MHV2 + UNIFAC		MHV2 + mod UNIFAC		MHV2 + new UNIFAC		
p/kPa	σ_y	σ_p/kPa	σ_y	σ_p/kPa	σ_y	σ_p/kPa	ref
101.3	0.041	2.8	0.015	2.4	0.020	2.7	Cervenkova and Boublik, 1984
101.3	0.018	0.90	0.012	2.5	0.006	0.97	Palczewska-Tulinksa and Wyrzykowska-Stankiewicz, 1990

[a] For the isothermal data obtained in this work, σ_y is the standard deviation between the calculated vapor compositions and those obtained by means of the Barker method.

Conclusions

Vapor−liquid equilibrium data are reported for methanol + TAME at three temperatures. Deviations from Raoult's law are positive, and the system forms an azeotrope. The agreement with previously reported data is good. Predictions obtained by means of several UNIFAC model versions were very accurate. The combination of the SRK EOS with these UNIFAC model versions also leads to good predictions. The inclusion of the EOS in the MHV2 + UNIFAC or new UNIFAC models improves the accuracy of the predictions as the temperature increases. This conclusion is also valid for the prediction of the azeotropic coordinates.

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Received for review November 28, 1995. Accepted February 2, 1996.[⊗] This work was funded by the Spanish Ministry of Education, Project DGICYT PB-94-0320 and PB-93-0448. F.M. acknowledges the European Union for its support through an HCM grant.

JE950300+

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.